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(54) Title: LIQUID ACCELERATOR

(57) Abstract: To provide a liquid accelerator which excels in its accelerating effect, thick-coating capability, strength development characteristics and the workability of concrete spray nozzle even for concrete with a relatively low cement content per unit volume, and which also excels in storage stability at low temperatures and high temperatures for a long period of time. A liquid accelerator composed of a fluoride-containing aqueous aluminum complex which is obtained through the reaction of aluminum sulfate and hydrofluoric acid, aluminum hydroxide, and phosphorous acid and/or organic acid salts thereof.

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Liquid accelerator

Description

The present invention relates to a liquid accelerator. Specifically, the present invention relates to a liquid accelerator which excels in its accelerating effect, thick-coating capability, strength development characteristics, and the workability of concrete-spray nozzle even for concrete with a lower cement content per unit volume (about 360 kg/m³) with a smaller amount of usage than that of conventional products, and also excels in the storage stability at lower and higher temperatures.

Conventionally, to prevent the collapses of exposed terrain surfaces such as a slope face and a tunnel excavation, spraying processes have been used in which accelerated mortar or concrete which is prepared by adding an accelerator to a cement composition such as mortar and concrete is sprayed on the spray surface. Generally, as the accelerator, alkali metal salts (sodium and potassium) of aluminate, silicic acid, carbonic acid, etc. have been widely used. Since these compounds have strong alkalinity, they have adverse effects on the human body in the environment of spray operation; for example, they may attack the skin and cause eye inflammation or corneal corrosion thereby impairing visual acuity.

Moreover, alkaline accelerators containing alkali metals such as sodium or potassium may pose the risk of inducing an alkali-aggregate reaction with the aggregates in concrete and, therefore, are not preferable in the viewpoint of durability of the concrete.

Moreover, since sprayed concrete generally includes a large cement content per unit volume thereby introducing a large quantity of alkali (sodium and potassium) from the cement and, in addition to it, has a high ratio of fine aggregates, there is a high probability of causing an alkali-aggregate reaction. Thus, when a reactive aggregate was used for sprayed concrete, there was a high risk of causing cracks in the concrete after it was cured thereby impairing the durability. As the countermeasure of this, attempts have been made to use aggregates which would not contribute to the alkali-aggregate reaction or to use low-alkali type cement; however, it was difficult to fully prevent the problem.

Under the current circumstances as described above, acidic liquid accelerators composed of aluminum sulfate, aluminum hydroxide, and the fluorides of aluminum have been proposed.

For example, a concrete accelerator consisting of an acidic or basic solution of aluminum, lithium silicate, and lithium aluminate has been proposed (see, for example, patent document 1). Moreover, an accelerator being free of alkalis and chlorides and consisting of nitrate, sulfate, glycolate, lactate, or the like of aluminum, a complex forming agent, and a corrosion inhibitor has been proposed (see, for example, patent document 2).

Furthermore, an accelerator that contains water soluble fluoride and does not contain aluminum salts, sulfates, alkali metals and chlorides has been proposed (see, for example, document 3). Furthermore, a liquid accelerator containing aluminum, sulfur, sodium, and fluorine has been proposed (see, for example, patent document 4). There has been further proposed an accelerator that consists of a fluoride-containing aqueous aluminum salt, which is obtained through the reaction between the aluminum hydroxides or aluminum oxides and hydrofluoric acid, and a sulfate-containing aqueous aluminum salt such as aluminum sulfate and basic aluminum sulfate, and that does not contain alkali metals and chlorides (see, for example, patent document 5).

However, the above described technologies have not provided a liquid accelerator having a sufficient accelerating effect and solution stability. The present inventors has focused their attention on the effects of alkali metals for improving early strength development characteristics of concrete, and proposed, in Japanese Patent Application No.2003-62114, a liquid accelerator that contains, as total alkali, 1 to 8.5% of alkali metal salts such as aluminum sulfate, alkanolamine, alkylene diamine, hydrofluoric acid, and alkali metal salts such as sodium hydroxide, potassium hydroxide, sodium carbonate, potassium carbonate, sodium sulfate, potassium sulfate. However, although this liquid accelerator excelled in its accelerating effect and early strength development characteristics for concrete compositions with a higher cement content per unit volume, it had a problem in that its acceleration performance was insufficient in concrete compositions with a lower cement content and it had a tendency to precipitate crystals at lower temperatures thereby degrading solution stability.

[Patent document 1] Jp,A2001-130935.

[Patent document 2] Jp,A2001-180994.

[Patent document 3] Jp,A2002-29801.

[Patent document 4] Jp,A2002-47048.

[Patent document 5] Jp,A2002-80250.

[Disclosure of the Invention]

[Problem to be Solved by the Invention]

Accordingly, it is an object of the present invention to provide a liquid accelerator which excels in its accelerating effect, thick-coating capability, strength development characteristics, and the workability of concrete-spray nozzle even for concrete with a lower cement content per unit volume, and also excels in the storage stability at lower and higher temperatures for a longer period of time.

[Means for Solving the Problem]

The present inventors have conducted eager investigation to solve the above described problems and have found that all those problems may be solved by using a liquid accelerator containing a fluoride-containing aqueous aluminum complex, aluminum hydroxide, and phosphorous acid, thereby eventually completing the present invention.

Thus, the present invention relates to a liquid accelerator composed of a fluoride-containing aqueous aluminum complex, which is obtained through the reaction between aluminum sulfate and hydrofluoric acid, aluminum hydroxide, and phosphorous acid and/or organic acid salts thereof.

The present invention also relates to the above described liquid accelerator in which aluminum compounds and hydrofluoric acid are used in an A/F ratio of 0.35 to 4.5, where the A/F ratio is the ratio of the number of moles of Al_2O_3 equivalent (A) to that of F^- equivalent (F).

The present invention also relates to the above described liquid accelerator in which aluminum compounds and sulfuric acid compounds are used in an A/S ratio of 0.38 to 0.60, where the A/S ratio is the ratio of the number of moles of Al_2O_3 equivalent (A) to that of SO_3 equivalent (S).

Furthermore, the present invention relates to the above described liquid accelerator in which total alkali is less than 1%.

The present invention further relates to the above described liquid accelerator in which 15 to 35% by mass of aluminum sulfate, 1 to 5% by mass of hydrofluoric acid, less than 20% by mass of aluminum hydroxide, and 0.5 to 5% by mass of phosphorous acid and/or organic acid salts thereof are used for the total amount of the liquid accel-

erator.

The present invention further relates to the above described liquid accelerator in which oxalic acid and/or a metallic salt thereof are contained.

The present invention further relates to the above described liquid accelerator in which 0.5 to 10% by mass of oxalic acid and/or a metallic salt thereof are used for the total amount of the liquid accelerator.

The present invention further relates to the above described liquid accelerator wherein the source of SO_3 is one or more kinds of sulfuric acid compounds selected from the group consisting of sulfuric acids, aluminum sulfates, lithium sulfates, sodium sulfates, and potassium sulfates.

The present invention further relates to the above described liquid accelerator wherein one or more members selected from the group consisting of C_1 to C_{10} organic monocarboxylic and dicarboxylic acids and metallic salts thereof are contained.

The present invention further relates to the above described liquid accelerator wherein one or more members selected from the group consisting of alkanolamine, alkylene diamine, and alkylene triamine are contained.

The present invention further relates to the use of the above described liquid accelerator for sprayed mortar or concrete applied to a dry or wet spraying process.

The present invention further relates to a process of dry or wet spraying wherein the above described liquid accelerator is added to a cement composition such as mortar or concrete in a transport pipe, a watering nozzle, or a spray nozzle either directly to the mixture by means of an accelerator feed device, or to the water content.

The present invention further relates to a process of dry or wet spraying characterized in that the above described liquid accelerator is added to base mortar or concrete which is added with a high-range AE water-reducing agent and/or a retarder of polycarbonic acid base and which is applied to the spraying process.
[Advantages of the Invention]

The liquid accelerator of the present invention can, by being added with phosphorous acid and/or organic acid salts thereof, provide excellent accelerating effect,

thick-coating capability, strength development characteristics, as well as the workability of concrete-spray nozzle even for concrete with a lower cement content per unit volume with a smaller amount of usage than that of conventional products, and also can provide excellent storage stability at lower and higher temperatures for a longer period of time. Further, the liquid accelerator of the present invention can enhance its effect as a liquid accelerator by being prepared, in addition to in the above described conditions, in a specific A/F ratio (molar ratio) or a specific A/S ratio (molar ratio), or added with oxalic acid and/or metallic salts thereof.

Since the accelerator of the present invention utilizes a fluoride-containing aqueous aluminum complex and thereby provides a good workability in spraying without excessively raising the early accelerating effect, it makes it possible to prevent the exfoliation of concrete during concrete spraying and apply a thick coating of concrete.

Moreover, since the above described fluoride-containing aqueous aluminum complex is obtained by adding hydrofluoric acid to aluminum sulfate, the accelerator of the present invention can be prepared by using less hydrofluoric acid than conventional methods in which aluminum compounds other than aluminum sulfate are used, and is therefore more economical and less hazardous in its preparation.

[The Best Mode for Carrying out the Invention]

Hereinafter, the present invention will be described in more detail.

Aluminum sulfate to be used in the present invention may be one which is generally used as accelerating agent, and it may be either fully or partly hydrated. A typical grade thereof is 17% aluminum sulfate ($\text{Al}_2(\text{SO}_4)_3 \cdot 14.3\text{H}_2\text{O}$) (referred to as such because of the aluminum oxide content) and, when using a different grade, a proper quantity may be calculated based on this grade. Also, it is preferable that aluminum sulfate is contained as $\text{Al}_2(\text{SO}_4)_3$ in an amount of 15 to 35% by mass of the total liquid accelerator.

The hydrofluoric acid to be used in the present invention is generally used as a HF aqueous solution of about 40 to 55% by mass. And the proportion of hydrofluoric acid (as HF) to be reacted with aluminum sulfate is preferably 1 to 5% by mass of the total liquid accelerator.

The present invention utilizes a fluoride-containing aqueous aluminum complex, which is obtained through the reaction between aluminum sulfate and hydrofluoric acid wherein preferably 15 to 35% by mass of aluminum sulfate is reacted with 1 to 5% by mass of hydrofluoric acid, and which would provide a good solution stability at low temperatures for a long term.

Since the above described fluoride-containing aqueous aluminum complex is obtained by adding hydrofluoric acid to aluminum sulfate unlike a conventional manner in which aluminum compounds are added to hydrofluoric solution, there is little heat of reaction generated and its manufacturing is less hazardous and safer.

The aluminum hydroxide to be used in the present invention may be amorphous aluminum hydroxide that is commonly used as accelerating agent, and is preferably contained up to 20% by mass of the liquid accelerator. It is also possible to use inexpensive crystalline aluminum hydroxides; however, they degrade the solution stability at low temperatures due to their low solubility and therefore cannot provide the same level performance as that of the amorphous type.

The liquid accelerator of the present invention is prepared such that aluminum compounds and hydrofluoric acid are contained preferably in an A/F ratio (molar ratio) of 0.35 to 4.5 and more preferably 0.45 to 2.0, where the A/F ratio is the ratio of the number of moles of Al_2O_3 equivalent (A) to that of F⁻ equivalent (F). When the ratio of $\text{Al}_2\text{O}_3/\text{F}^-$ is within these ranges, the liquid accelerator will have an excellent very-early delaying effect and accelerating effect thereby improving the thick-coating capability and the strength development characteristics of sprayed concrete and also preventing the deposit of concrete onto the inner surface of the spray nozzle. The adjustment of A/F (molar ratio) in the present invention may be performed by means of the contents of aluminum sulfate, hydrofluoric acid and aluminum hydroxide; however, other aluminum compounds can also be used.

The liquid accelerator of the present invention is added with phosphorous acid and/or organic acid salts thereof to prevent the concrete from becoming clouded at high temperatures and improve its storage stability. As used in the present invention, one or more kinds selected from the group consisting of phosphorous acid and/or organic acid salts thereof are preferably 0.5 to 5% by mass,

more preferably 1.5 to 3% by mass of the total amount of the liquid accelerator.

The liquid accelerator of the present invention is prepared such that aluminum compounds and sulfuric acid compounds are contained in an A/S ratio of 0.38 to 0.60 and more preferably 0.40 to 0.55, where the A/S ratio is the ratio of the number of moles of Al_2O_3 , equivalent (A) to that of SO_3 , equivalent (S). When the A/S ratio is within these ranges, the liquid accelerator exerts an excellent early accelerating effect and strength development characteristic. Moreover, as used in the liquid accelerator of the present invention, the source of SO_3 for controlling A/S includes sulfuric acid compounds such as sulfuric acid, aluminum sulfate and lithium sulfate, and one or more kinds of sodium sulfate and potassium sulfate may be used in an amount such that the total alkali is less than 1%. The preferable proportion of the sulfuric acid compounds is 15 to 35% by mass of the total liquid accelerator.

In the liquid accelerator of the present invention, the total alkali amount is preferably less than 1% and more preferably less than 0.5%. The total alkali (%) as used in the present invention is expressed by $\text{Na}_2\text{O}_{\text{eq}}$ = sodium oxide (Na_2O) + 0.658 potassium oxide (K_2O). When the total alkali in the liquid accelerator is within this range, the liquid accelerator exhibits good solution stability at low temperatures, does not cause crystal precipitation, and favorably behaves against alkali aggregation reaction.

Further, the liquid accelerator of the present invention preferably utilizes 15 to 35% by mass of aluminum sulfate, 1 to 5% by mass of hydrofluoric acid, not more than 20% by mass of aluminum hydroxide, and 0.5 to 5% by mass of phosphorous acid and/or organic acid salts thereof for the total liquid accelerator.

The liquid accelerator of the present invention may contain oxalic acid and/or metallic salts thereof for the purpose of improving the very early delaying effect of concrete, and the oxalic acid and/or metallic salts thereof can be used to adjust the very early delaying effect in accordance with the change in the very early delaying effect due to the difference in the materials used at the work site. As used in the present invention, one or more kinds selected from the group consisting of oxalic acid and/or metallic salts thereof are preferably 0.5 to 10% by mass of the total liquid accelerator.

The liquid accelerator of the present invention preferably utilizes 15 to 35% by mass of aluminum sulfate, 1 to 5% by mass of hydrofluoric acid, not more than 20% by mass of aluminum hydroxide, 0.5 to 5% by mass of phosphorous acid and/or organic acid salts thereof, and 0.5 to 10% by mass of oxalic acid and/or metallic salts thereof for the total liquid accelerator.

The liquid accelerator of the present invention may contain C₁ to C₁₀ organic monocarboxylic and dicarboxylic acids and one or more metallic salts thereof for the purpose of improving the early strength of concrete. The C₁ to C₁₀ organic monocarboxylic and dicarboxylic acids and metallic salts thereof may be preferably formic acid, oxalic acid, and glycol acid as well as the metallic salts thereof, and other acids such as acetic acid, propionic acid, succinic acid, citric acid and tartaric acid may also be used. Moreover, a preferable proportion of these components is 1 to 10% by mass, and more preferably 2 to 8% by mass of the total liquid accelerator

Furthermore, to improve the solution stability, the liquid accelerator of the present invention may utilize the combination of one or more kinds of alkanolamine, alkylene diamine, and alkylene triamine. These components are preferably ethylenediamine, ethylenetriamine, diethanolamine or triethanolamine, and more preferably diethanolamine. These components may be contained preferably in a proportion of 0.1 to 10% by mass, and more preferably 0.1 to 8% by mass of the total liquid accelerator.

The liquid accelerator of the present invention can be prepared in a simple manner by mixing in any order and stirring the above explained components to eventually have a pH of 2 to 8 and contain 40 to 70% by mass of water.

The suitable use of the liquid accelerator of the present invention is to add the liquid accelerator of the present invention into a cement composition such as mortar or concrete applied to conventional dry or wet spraying process. In using the liquid accelerator of the present invention, it may be added in an amount of 5 to 12% by mass with respect to the mass of the cement in the cement composition, although the amount will vary depending on the applications.

The present invention is a process of dry or wet

spraying wherein the above described liquid accelerator is added to a cement composition such as mortar or concrete inside a transfer pipe, a watering nozzle, or a spraying nozzle either directly to the mixture by means of an accelerator feed device, or to the water content.

Moreover, the present invention is a process of spraying wherein the liquid accelerator is added by a method shown in [0030] to the base mortar or concrete to be applied to the spraying process wherein the base mortar or concrete is added with a high-range AE water-reducing agent and/or a retarder of polycarboxylic acid base.

The high-range AE water-reducing agent of polycarboxylic acid base of the present invention may be any commercially available one for general-purpose uses. Commercially available high-range AE water-reducing agents of polycarboxylic acid base includes: polycarboxylic acid base cement water-reducing agent having polyalkylene oxide group such as one in JP,A,58-38380 (copolymer of polyethylene glycol methacrylate and methacrylic acid), JP,A,62-70250 (copolymer of polyethylene glycol methacrylate, methacrylic acid, and amino-compound adduct having polyalkylene oxide of unsaturated carboxylic acid); and ones in JP,A,05-213644 (copolymer of polyethylene glycol methacrylate and methacrylic acid), JP,A,05-238795 (copolymer selected from polyalkylene glycol diester base monomers having unsaturated bonds, acrylic acid base monomers and polyalkylene glycol monoester monomers having unsaturated bond) JP,A,09-286645 (copolymer of polyethylene glycol, of which oxyethylene group has different chain lengths of 1 to 10 and 11 to 100, and methacrylic acid), Japanese Patent No.2541218 (copolymer of polyoxyalkylene derivatives and maleic anhydride) JP,A,07-215746 (copolymer of polyoxyalkylene derivatives and maleic anhydride), JP,A,05-310458 (copolymer of alkenyl ether and maleic anhydride), JP,A,04-74748 (copolymer of olefins of carbon number 2 to 8 and ethylene-base unsaturated dicarboxylic anhydride), JP,A,62-83344 (metallic complex with polyacrylic acid or copolymers of olefins of carbon number 2 to 8 and ethylene-base unsaturated dicarboxylic acid etc.), JP,A,2001-180998 (concrete admixture which contains copolymer mixture which is obtained by copolymerizing a specific monomer (A) such as ethylene-base unsaturated carboxylic derivatives having polyoxyalkylene group, and another specific monomer (B) such as (metha) acrylic acid, and in which the molar ratio (A)/(B) is changed at least once during the reaction), JP,B,06-99169 (polyethylene-imine com-

pound consisting of poly(acidic group substituted alkyl group and/or acidic group substituted acyl group)polyethylene-imine and poly(acidic group substituted alkyl group and carbamoyl alkyl group)polyethylene-imine), JP,A,08-283350 (oxyalkyleneglycol-alkenyl ether and unsaturated dicarboxylic acid derivatives and vinyl-base polyalkyleneglycol compounds, polysiloxane compounds or ester compounds), JP,A,2000-351820 (containing a copolymer based on unsaturated monocarboxylic derivatives or dicarboxylic derivatives and oxyalkyleneglycol-alkenyl ether group).

The retarder in the present invention may be exemplified by phosphonic acid derivatives selected from the group consisting of aminotri(methylenephosphonic acid), aminotri(methylenephosphonic acid) 5 sodium salt, 1-hydroxyethylidene-1,1-diphosphonic acid, 1-hydroxyethylidene-1,1-diphosphonic acid 4 sodium salt, ethylenediaminetetra(methylenephosphonic acid), ethylenediaminetetra(methylenephosphonic acid) calcium/sodium salt, hexamethylene-diaminetetra(methylenephosphonic acid), hexamethylene-diaminetetra(methylenephosphonic acid) potassium salt, diethylenetriaminepenta(methylenephosphonic acid), and diethylenetriaminepenta(methylenephosphonic acid) sodium salt; and hydroxycarbonic acid and the salts thereof selected from salicylic acid, citric acid, lactic acid, gluconic acid, tartaric acid, muconic acid, and glucoheptanoic acid. Preferable retarder may be exemplified by ones containing phosphonic acid derivatives and citric acid and/or gluconic acid, and the salts thereof.

[Examples]

Hereinafter, the present invention will be explained in detail referring to test examples 1 to 5. The materials, the composition of the mortar, and the measurement method used for the tests are shown in Table 1, and A/F, A/S, components and compositions of the comparative samples and inventive samples used as the accelerator for the test are shown in Table 2.

[Table 1]

Cement	Ordinary portland cement manufactured by TAIHEIYO CEMENT Co.
Fine aggregate	OI River System pit sand
High-range AE water-reducing agent	NT-1000 (Manufactured by NMB Co., Ltd.) Polycarboxylic acid base
Comparative sample 1 - 3	Used in the amount of 9% by weight for the cement mass

Inventive sample 1 - 14		Used in the amount of 9% by weight for the cement mass
Mortar composition 1	Water/cement ratio (W/C) = 40%, sand/cement ratio (S/C) = 2.1	
Mortar composition 2	Water/cement ratio (W/C) = 50%, sand/cement ratio (S/C) = 2.45	
Measurement method	Setting time	Starting time: Time needed for the Proctor penetration resistance value to reach 3.5 N/mm ²
	Compressive strength	In accordance with JIS R 5201
	Very early delaying effect	By visual observation

[Table 2]
Table 2

Accelerator type	A/F	A/S	Composition of accelerator (%)					
			Al ₂ (SO ₄) ₃	Al(OH) ₃	HF	(COOH) ₂ □ 2H ₂ O	H ₃ PO ₃	Na ₂ SO ₄
Comparative sample 1	0.8 4	0.3 8	18.2	5.4	2. 1	6.7	0	10.0
Comparative sample 2	0.8 6	0.5 4	26.0	7.2	2. 8	0	0	0
Comparative sample 3	0.8 6	0.5 4	26.0	7.2	2. 8	3.0	0	0
Inventive sample 1	0.8 6	0.5 4	26.0	7.2	2. 8	0	2.0	0
Inventive sample 2	0.8 6	0.5 4	26.0	7.2	2. 8	3.0	1.0	0
Inventive sample 3	0.8 6	0.5 4	26.0	7.2	2. 8	3.0	2.0	0
Inventive sample 4	2.1 6	0.4 5	27.5	4.3	1. 0	0	1.0	0
Inventive sample 5	1.0 8	0.4 5	27.5	4.3	2. 0	0	1.0	0
Inventive sample 6	0.7 2	0.4 5	27.5	4.3	3. 0	0	1.0	0
Inventive sample 7	0.5 4	0.4 5	27.5	4.3	4. 0	0	1.0	0
Inventive	0.4	0.4	27.5	4.3	5.	0	1.0	0

sample 8	3	5			0			
Inventive sample 9	0.8	0.3	27.2	1.1	2.	0	1.0	0
	5	5			0			
Inventive sample 10	0.8	0.4	24.7	2.2	2.	0	1.0	0
	5	0			0			
Inventive sample 11	0.8	0.4	23.2	3.2	2.	0	1.0	0
	5	4			1			
Inventive sample 12	0.8	0.5	21.2	4.7	2.	0	1.0	0
	5	0			2			
Inventive sample 13	0.8	0.5	20.0	5.6	2.	0	1.0	0
	5	4			2			
Inventive sample 14	0.8	0.6	16.7	8.2	2.	0	1.0	0
	5	9			4			

(Test example 1)

Test results for the case in which phosphorous acid and oxalic acid were added to the liquid accelerator according to mortar composition 2 are shown in Table 4. It is clearly seen from Table 4 that the inventive samples 2 and 3 showed an improved accelerating effect and early strength development characteristics.

(Test example 2)

Using the concrete composition shown in Table 3, a thick-coating capability test of sprayed concrete was conducted. Concrete spraying was conducted onto the top end of a tunnel until an exfoliation occurred and the average thickness of the sprayed concrete was measured. Also the state inside the concrete spray nozzle was checked by visual observation. The amount of accelerator used was 9% by weight with respect to the mass of cement.

[Table 3]

W/C (%)	s/a	Mass per unit volume (kg/m ³)			
		W	C	S	G
56	60	202	360	1020	699

As shown in Table 4, inventive samples 2 and 3, in which phosphorous acid and oxalic acid were used in combination, showed improvements in the thick-coating capability of sprayed concrete. Also, the state inside the concrete spray nozzle was good as no cured concrete remained on the inner wall surface of the nozzle. The inventive sample 1 showed an improvement in the thick-coating capability of sprayed concrete; but a small amount of cured concrete was

observed on the inner wall surface of the concrete spray nozzle. Neither of the comparative sample 1 and 2 showed an improvement in the thick-coating capability.

[Table 4]

Accelerator Type	A/S	A/S	Al ₂ O ₃ (%)	SiO ₂ (%)	HF (%)	(COOH) ₂ H ₂ O (%)	H ₂ O (%)	Mortar Test		Concrete Test			
								Setting time (min.-sec.)	Compressive strength (N/mm ²) 3 hours 24 hours	Very early delaying effect	Sprayed thickness (cm)	Inner surface or nozzle	
Comparative sample 1	0.84	0.38	9.0	22.2	2.1	6.7	-	25-00	0.54	4.24	Excessive	15	o
Comparative sample 2	0.86	0.54	13.5	21.9	2.8	-	-	6-30	0.61	2.82	Insufficient	20	x
Comparative sample 3	0.86	0.54	12.5	21.9	2.8	3.0	-	5-00	0.81	2.72	Good	28	o
Inventive sample 1	0.86	0.54	12.5	21.9	2.8	-	2.0	5-30	0.83	2.85	Insufficient	30	□
Inventive sample 2	0.86	0.54	12.5	21.9	2.8	3.0	1.0	5-00	0.89	2.75	Good	31	o
Inventive sample 3	0.86	0.54	12.5	21.9	2.8	3.0	2.0	5-00	0.72	3.12	Good	37	o

Evaluation method of the state of the inner wall surface of the spray nozzle

o: No cured-concrete on the wall surface

□: Small amount of cured concrete on the wall surface

x: Blocked by the cured concrete on the wall surface

(Test example 3)

The results of the solution stability test are shown in Table 5. The liquid accelerators were stored for two months under temperature conditions of 2, 5, 20, 30, and 40 °C. The inventive samples showed good solution stability for a long period of time at low temperatures and high temperatures.

[Table 5]

Accelerator Type	Environment temperature (°C)	Number of days				
		1 week	2 weeks	3 weeks	1 month	2 months
Comparative sample 1	2	o	o	X	X	X
	5	o	o	o	X	X
	20	o	o	o	o	o
	30	o	o	o	o	o
	40	o	o	o	o	o
Comparative sample 2	2	o	o	o	o	o
	5	o	o	o	o	o
	20	o	o	o	o	o
	30	o	▲	▲	▲	▲
	40	▲	▲	▲	▲	▲
Comparative sample 3	2	o	o	o	o	o
	5	o	o	o	o	o
	20	o	o	o	o	o
	30	o	▲	▲	▲	▲
	40	▲	▲	▲	▲	▲
Inventive sample 1	2	o	o	o	o	o
	5	o	o	o	o	o
	20	o	o	o	o	o
	30	o	o	o	o	o
	40	o	o	o	o	o
Inventive sample 2	2	o	o	o	o	o
	5	o	o	o	o	o
	20	o	o	o	o	o
	30	o	o	o	▲	▲
	40	o	o	▲	▲	▲
Inventive sample 3	2	o	o	o	o	o
	5	o	o	o	o	o
	20	o	o	o	o	o
	30	o	o	o	o	o
	40	o	o	o	o	o

Evaluation method: o good, ▲ clouded, × crystal pre-

cipitation

(Test example 1)

The results of the mortar test in mortar composition 1 are shown in Table 7 for the cases in which the A/F ratio of the liquid accelerator was varied from 0.43 to 2.16. As seen in Table 7, when the A/F of the liquid accelerator was 0.43, the 24-hour strength development was small; when A/F was 2.16, the start time was delayed; and when in a range of 0.54 to 1.08, well balanced development characteristics was seen in the start time, the 3-hour material age, and the 24-hour material age.

The results of the mortar test in mortar composition 1 are shown in Table 8 for the cases in which the A/S ratio of the liquid accelerator was varied from 0.35 to 0.69. As seen in Table 8, when the A/S of the liquid accelerator was 0.35, the start time was delayed; when A/S was 0.69, the 24-hour strength development was small; and when in a range of 0.40 to 0.54, well balanced development characteristics was seen in the start time, the 3-hour material age, and the 24-hour material age.

(Test example 2)

Using the concrete compositions shown in Table 6, a thick-coating capability test of sprayed concrete was conducted. Concrete spraying was conducted on the top end of a tunnel until an exfoliation occurred and the average thickness of the sprayed concrete was measured. Also, the state of the concrete spray nozzle was checked by visual observation. The use amount of accelerators was 9% by weigh with respect to the cement mass.

[Table 6]

W/C (%)	s/a	Mass per unit volume (kg/m ³)			
		W	C	S	G
42.2	60	190	450	991	678

As shown in Table 7, when the A/F of the accelerators was in a range of 0.54 to 1.08, improvements in the thick-coating capability were observed and the state of the concrete spray nozzle was in a good condition as no cured concrete remained on the inner wall surface of the nozzle.

[Table 7]

Accelerator Type	A/F	A/S	Al ₂ O ₃ (%)	SO ₄ ²⁻ (%)	HF (%)	H ₃ PO ₃ (%)	Mortar Test			Concrete Test		
							Setting time (min.-sec.)	Compressive strength (N/mm ²)	Very early delaying effect	Sprayed thickness (cm)	Inner surface of nozzle	
Inventive sample 4	2.16	0.45	11.0	23.1	1.0	1.0	10-00	1.05	Insufficient	15	□	
Inventive sample 5	1.08	0.45	11.0	23.1	2.0	1.0	8-30	1.27	Good	30	o	
Inventive sample 6	0.72	0.45	11.0	23.1	3.0	1.0	8-00	1.28	Good	33	o	
Inventive sample 7	0.54	0.45	11.0	23.1	4.0	1.0	8-00	1.33	Good	25	o	
Inventive sample 8	0.43	0.45	11.0	23.1	5.0	1.0	8-00	1.41	Excessive	20	o	

Evaluation method of the state of the inner wall surface of the spray nozzle

o: No cured concrete on the wall surface

□: Small amount of cured concrete on the wall surface

x: Blocked by the cured concrete on the wall surface

[Table 8]

Accelerator Type	A/F	A/S	Al ₂ O ₃ (%)	SO ₄ ²⁻ (%)	HF (%)	H ₃ PO ₃ (%)	Mortar Test		
							Setting time	Compressive strength (N/mm ²)	
							Start (min.- sec.)	3 hours	24 hours
Inventive sample 9	0.85	0.35	8.5	22.9	2.0	1.0	14-00	1.15	13.4
Inventive sample 10		0.40	8.8	20.7	2.0		11-30	1.29	12.7
Inventive sample 11		0.44	9.0	19.5	2.1		10-30	1.34	12.6
Inventive sample 12		0.50	9.4	17.8	2.2		10-00	1.45	10.1
Inventive sample 13		0.54	9.6	16.8	2.2		9-00	1.62	8.89
Inventive sample 14		0.69	10.3	14.1	2.4		7-30	1.53	5.94

[Industrial Applicability]

According to the present invention, there is provided a liquid accelerator which excels in its accelerating effect, thick-coating capability, strength development characteristics, and the workability of concrete spray nozzle for compositions of a low cement content ($C = 360$ to 390 kg/m^3) and which also excels in the storage stability at low temperatures and high temperatures for a long period of time.

Claims

1. A liquid accelerator composed of a fluoride-containing aqueous aluminum complex, which is obtained through the reaction of aluminum sulfate and hydrofluoric acid, aluminum hydroxide, and phosphorous acid and/or organic acid salts thereof.
2. The liquid accelerator according to claim 1, wherein aluminum compounds and hydrofluoric acid are used in an A/F ratio of 0.35 to 4.5, where the A/F ratio is the ratio of the number of moles of Al_2O_3 equivalent (A) to that of F equivalent (F).
3. The liquid accelerator according to claim 1 or 2, wherein aluminum compounds and sulfuric compounds are used in an A/S ratio of 0.38 to 0.60, where the A/S ratio is the ratio of the number of moles of Al_2O_3 equivalent (A) to that of SO_3 equivalent (S).
4. The liquid accelerator according to any of claims 1 to 3, wherein total alkali is less than 1 %.
5. The liquid accelerator according to any of claims 1 to 4, characterized in that 15 to 35 % by mass of aluminum sulfate, 1 to 5 % by mass of hydrofluoric acid, less than 20 % by mass of aluminum hydroxide, and 0.5 to 5 % by mass of phosphorous acid and/or organic acid salts thereof are used for the total amount of the liquid accelerator.
6. The liquid accelerator according to any of claims 1 to 5, wherein oxalic acid and/or metallic salts thereof are contained.
7. The liquid accelerator according to claim 6, characterized in that 0.5 to 10 % by mass of oxalic acid and/or metallic salts thereof are used for the total amount of the liquid accelerator.
8. The liquid accelerator according to any of claims 1 to 7, wherein the source of SO_3 is one or more kinds of sulfuric compounds selected from the group consisting of sulfuric acids, aluminum sulfates, lithium sulfates, sodium sulfates, and potassium sulfates.

9. The liquid accelerator according to any of claims 1 to 8, wherein one or more members selected from the group consisting of C_1 to C_{10} organic monocarboxylic and dicarboxylic acids and metallic salts thereof are contained.
10. The liquid accelerator according to any of claims 1 to 9, wherein one or more members selected from the group consisting of alkanolamine, alkylene diamine, and alkylene triamine are contained.
11. The use of the liquid accelerator according to any of claims 1 to 10 for sprayed mortar or concrete applied to a dry or wet spraying process.
12. A process of dry or wet spraying wherein the liquid accelerator according to any of claims 1 to 10 is added to a cement composition such as mortar or concrete in a transport pipe, a watering nozzle, or a spray nozzle either directly to the mixture by means of an accelerator feed device, or to the water content.
13. A process of dry or wet spraying characterized in that the liquid accelerator according to any of claims 1 to 10 is added to base mortar or concrete which is added with a high-range AE water-reducing agent and/or a retarder of polycarbonic acid base and which is applied to the spraying process.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/EP2005/012107

A. CLASSIFICATION OF SUBJECT MATTER
C04B40/00 C04B28/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C04B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data bases consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 1 167 317 A (SIKA SCHWEIZ AG) 2 January 2002 (2002-01-02) the whole document	1-4,6-13
X	WO 03/106375 A (CONSTRUCTION RESEARCH & TECHNOLOGY GMBH; ANGELSKAAR, TERJE; IWATA, RAI) 24 December 2003 (2003-12-24) the whole document	1-13
X,P	WO 2005/028398 A (CONSTRUCTION RESEARCH & TECHNOLOGY GMBH; ANGELSKAR, TERJE; IWATA, RAIT) 31 March 2005 (2005-03-31) the whole document	1-13
X,P	WO 2005/040059 A (MAPEI S.P.A.; MALTESE, CRISTIANO; PISTOLESI, CARLO; FERRARI, GIORGIO) 6 May 2005 (2005-05-06) the whole document	1,4,8-13

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

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Date of the actual completion of the international search

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

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